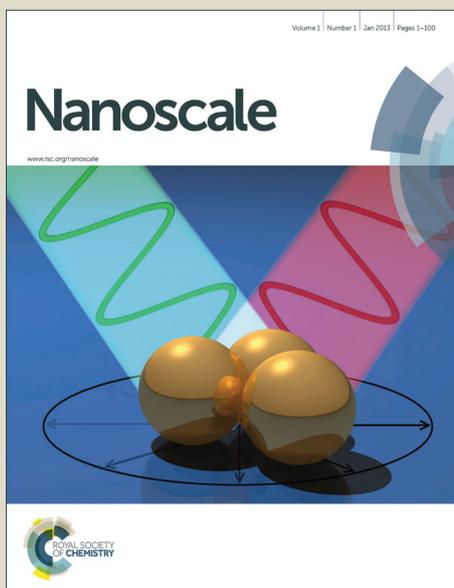


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COMMUNICATION**Superatom-atom super-bonding in metallic clusters: A new look to the mystery of Au₂₀ pyramid**Longjiu Cheng,^{*a} Xiuzhen Zhang,^a Baokang Jin,^a and Jinlong Yang^{*b}

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Using the super valence bond model, a generalized chemical picture for the electronic shells of Au₂₀ pyramid is given. It is found that Au₂₀ can be viewed as a superatomic molecule, of which its superatomic 16c-16e core (T) is in D³S hybridization bonded with four vertical Au atoms for molecule-like (TAu₄) electronic shell-closure. Based on such a superatom-atom bonding model, TX₄ (X = F, Cl, Br ...) are predicted to be very stable. Such a superatom-atom T-Au/T-X bonding enriches the continent of chemistry.

Au has the strongest relativistic effects among all elements, which results in strong *sd* hybridization and unique properties from other coin metals.¹ Small Au clusters display unique planar structures at about $N = 2-10$,² a transition from 2D to 3D structures at $N = 11-13$,³ flat cage at $N = 14-19$,⁴ pyramidal cage for Au₂₀,⁵ tubular structure for Au₂₆,⁶ golden fullerene for Au₃₂ and Au₇₂,^{7,8} and core-shell structure at $N = 33-38$.⁹

Among Au clusters, Au₂₀ cluster is very unique which possesses a pyramidal structure (*T_d*) far from spherical.⁵ It has a remarkably large energy gap (1.77 eV) between highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO), which is even larger than that of C₆₀ (1.57 eV).¹⁰ The large energy gap of Au₂₀ cage suggests that it is a highly inert and stable molecule and may have novel optical and catalytic properties.¹¹

Stability of metallic clusters is mainly determined by the electronic structure other than the atomic structure at a small size, which can be understood by the Jellium model. Jellium model¹² assumes a uniform background of positive charge of the cluster's atomic nuclei and the innermost electrons, in which valence electrons move and are subjected to an external potential. Thereby, the whole cluster can be viewed as a "superatom", and the appropriate aufbau rule of super shells for spherical alkali-metal clusters is $|1S^2|1P^6|1D^{10}2S^2|1F^{14}2P^6|...$ (Here upper letters represent super shells and lower letters for electronic shells of atoms). Based on such a superatomic shell model, exceptional stability is associated with the magic numbers 2, 8, 20, 40 ..., in good agreement with the observed experimental abundances of alkali-metal clusters in the gas phase, and the magic stability of icosahedral Al₁₃⁻ cluster.^{13,14}

For Au ($5d^{10}6s^1$) clusters, the full-filled $5d$ electrons are

mainly localized as lone-pairs (LPs) and $6s^1$ are free valence electrons. Due to the $6s$ character, the appropriate aufbau rule of super shells for spherical Au clusters is $|1S^2|1P^6|1D^{10}|2S^21F^{14}|2P^61G^{18}|...$, associated with magic numbers 2, 8, 18, 34, 58,¹⁵ Superatom theory has achieved great successes in the stability of many experimentally produced thiolate-protected gold nanoparticles, which can be understood by the magic numbers, such as Au₁₀₂(SR)₄₄ (58e),¹⁶ Au₆₈(SR)₃₄ (34e),¹⁷ Au₄₄(SR)₂₈²⁻ (18e),¹⁸ Au₂₅(SR)₁₈⁻ (8e),¹⁹ and Au₁₂(SR)₉⁺ (2e).²⁰ The large energy gap of Au₃₄ cluster viewed in experiments is also in agreement with the superatom shell model.²¹

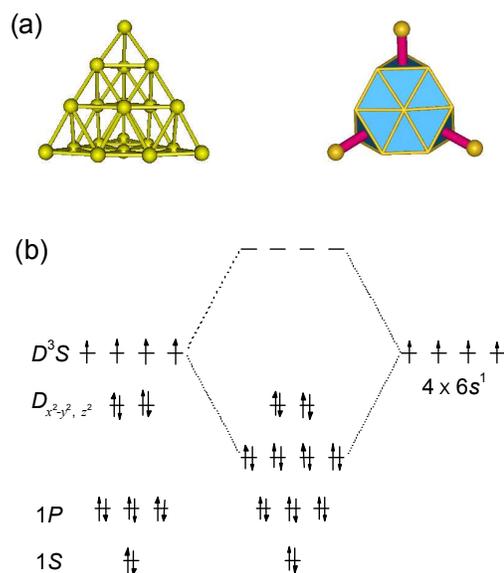


Figure 1. (a) Structure and superatomic-molecule models of Au₂₀ (TAu₄). (b) Schematic representation for the superatom-atom D³S-s bonding of Au₂₀ (TAu₄).

However, the above superatom aufbau rule is based on a spherical field associated with spherical cluster motifs. The shell orders for non-spherical clusters may not follow superatom aufbau rule. For example, the shell orders and magic numbers are much different in the ellipsoidal shell model.²² Pyramidal Au₂₀ is far from spherical, of which the 20 valence electrons disagree with the magic numbers in spherical Jellium shell model.

To understand the magic stability of Au₂₀ cage, King et al²³ thought that the 20 free electrons can be used to form a four-center-two-electron (4c-2e) bond in each of 10 tetrahedral cavities of the Au₂₀ cluster (four at vertices and six at edges).
 5 Later, such a conjugated 4c-2e bonding model²⁴ was confirmed by natural bonding orbital (NBO) analysis using the adaptive natural density partitioning (AdNDP)^{25,26} method (see Figure s1 in Supporting Information).

Recently, we proposed a super valence bond (SVB) model²⁷ to explain the electronic stability of non-spherical shells of metallic clusters. In SVB model, a non-spherical metallic cluster can be viewed as a superatomic molecule bonded by several spherical superatoms, of which atomic nuclei can be shared by neighboring superatoms. Valence electrons are
 10 mainly delocalized over the region of each superatom instead of the whole cluster volume, following the rule of Jellium model. The superatoms can be open-shell, and molecule-like shell-closure is achieved by sharing electron pairs between superatoms via super bonding. Based on SVB model,
 15 electronic stability of lithium clusters²⁷ and ligand-protected Au clusters²⁸ can be understood by superatom-superatom super bonding.

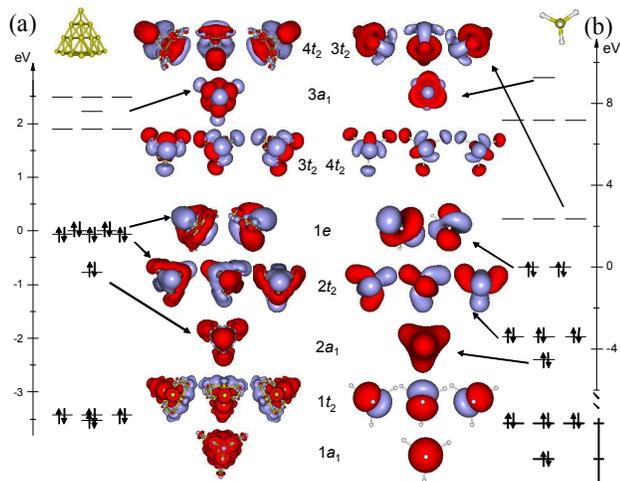


Figure 2. Comparison of the Kohn-Sham MO diagrams of
 25 (a) Au₂₀ (TAu₄) and (b) OsH₄.

To uncover the mystery of Au₂₀, we give a new physical insight into the electronic structure of Au₂₀ using the SVB model. As shown in Figure 1a, the truncated-tetrahedron Au₁₆ core of Au₂₀ pyramid is spherical enough and viewed as an
 30 open-shell 16e-superatom (abbreviated as T). Electronic shells of T (1S²1P⁶1D⁸) follow the rule of spherical Jellium model. Molecule-like electronic shell-closure is achieved by four superatom-atom super bonding (T-Au), and Au₂₀ can be viewed a superatomic molecule TAu₄. Figure 1b gives a
 35 schematic representation of the bonding pattern of TAu₄. The 1S²1P⁶ shells of T are super LPs of the inner core. The five 1D orbitals split into two sets in a tetrahedral field, a set of lower double-degenerate orbitals (1D<sub>x²-y², z²) and a set of higher triple-degenerate orbitals (1D_{xy, yz, zx}). The lower two
 40 1D_{x²-y², z²) orbitals are full-filled as super LPs. The higher three 1D_{xy, yz, zx} orbitals are in D³S hybridization with the 2S orbital. The four D³S super orbitals are bonded with four 6s¹ orbitals}</sub>

of the vertex Au atoms, splitting into four occupied lower bonding orbitals and four higher anti-bonding orbitals. Such a
 45 bonding pattern is analogous of a simple molecule OsH₄, where Os [5s²5p⁶(5d6s)⁸] is in d³s hybridization bonded with four H atoms.

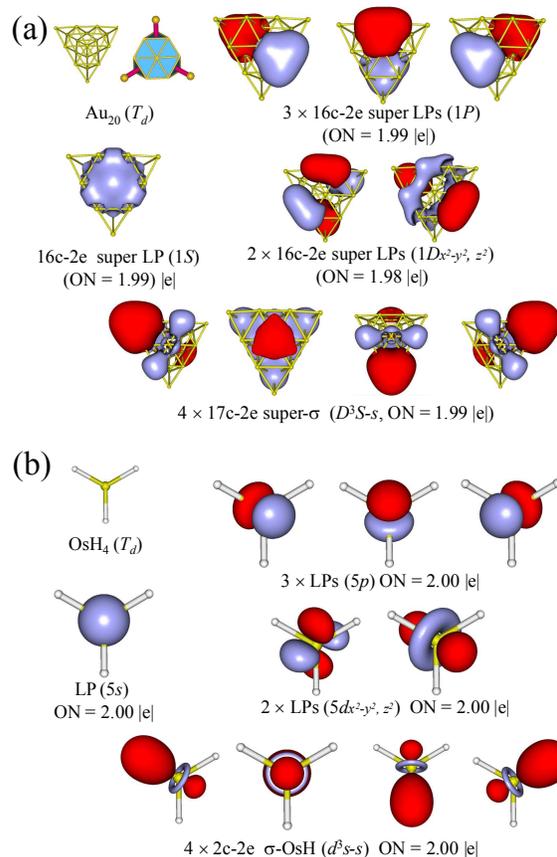


Figure 3. Structures and AdNDP localized natural bonding
 50 orbitals of (a) Au₂₀ (TAu₄) and (b) OsH₄.

To verify the superatom-atom super bonding in Au₂₀ (TAu₄), we give molecular orbital (MO) and chemical bonding analysis by density function theory (DFT) calculations. The generalized gradient approximation method
 55 by Tao-Perdew-Staroverov-Scuseria (GGA-TPSS),²⁹ with relativistic effective core potential basis set (LanL2DZ) is adopted in this study. The calculated energy gap of Au₂₀ under TPSS/LanL2DZ is 1.90 eV in good agreement with the experimental value (1.77 eV).⁵

Figure 2 compares the canonical Kohn-Sham MO diagrams of TAu₄ and OsH₄. As expected, electronic configurations and orbital shapes of TAu₄ are in good agreement with those of OsH₄. (1a₁)² and (1t₂)⁶ MOs correspond to 1S and 1P (5s and 5p) orbitals of T (Os). (1e)⁴ MOs corresponds to 1D<sub>x²-y², z²)²
 60 (5d_{x²-y², z²) orbitals of T (Os). (2a₁)²(2t₂)⁶ MOs correspond to four D³S-6s (d³s-1s) T-Au (Os-H) bonding orbitals. The four anti-bonding D³S-6s (d³s-1s) MOs are (3t₂)⁰(3a₁)⁰ for T-Au and (4t₂)⁰(3a₁)⁰ for Os-H.}</sub>

Chemical bonding analysis by AdNDP gives a more
 70 straightforward evidence for the superatom-atom bonding. As

shown in Figure 3a, AdNDP analysis reveals six 16c-2e super LPs of T (super $1S$, $1P_{x,y,z}$, $1D_{x^2-y^2, z^2}$) and four 17c-2e T-Au super σ -bonds in Au_{20} . Such a bonding framework of TAu_4 is analogous to that of OsH_4 , especially between the shapes of the T-Au (D^3S-s) and Os-H (d^3s-s) bonds (Figure 3b). Moreover, occupancy numbers (ONs) of the super LPs and T-Au super bonds are very close to the ideal value 2.0 |e| (ON > 1.98 |e|), indicating very high reliability.

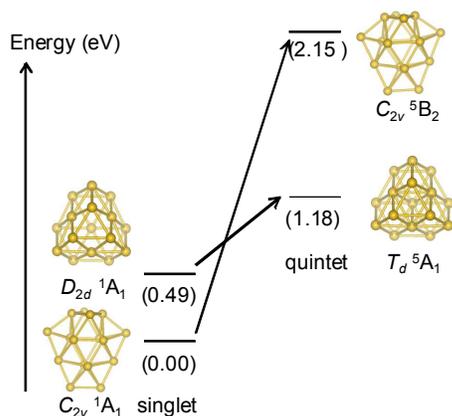


Figure 4. Energy levels of the singlet and quintet states of the flat cage and truncated tetrahedron motifs of Au_{16} .

In the formation of hybrid atomic orbitals, the atom is viewed as a point and is structure-free. However, the superatom has a 3D structure, and structural rearrangement may take place during the formation of hybrid super orbitals. As shown in Figure 4, the lowest-energy structure of Au_{16} is a C_{2v} flat cage⁴ in singlet state (1A_1). The singlet truncated tetrahedron remains a hollow T_d cage with minor distortion (D_{2d}) due to the Jahn-Teller effect,³⁰ and is 0.49 eV higher in energy. After D^3S hybridization before the formation of T-Au bonds, the quintet truncated tetrahedron retains exact T_d symmetry without Jahn-Teller distortion and the hybridization energy is only 0.69 eV. As a comparison, the quintet state is even 2.15 eV higher in energy than the singlet state for the flat cage structure. In Au_{20} (TAu_4) pyramid, the symmetry of geometry satisfies the symmetry of hybrid super orbitals, which may be the reason for its magic stability.

The four vertical Au atoms in Au_{20} can be replaced by other 1e-atoms. IA (H, Li, Na, and K) and other IB (Cu and Ag) elements can also form stable $Au_{16}M_4$ (TM_4) superatomic molecules with reasonably large HOMO-LUMO gaps and vertical ionic potentials (VIPs) (see Figure S2 in Supporting Information). In TM_4 superatomic molecules, T acts as a Lewis base in -4 charge state.

Based on the VB theory, Os atoms can act as a Lewis acid and bond with four halogens to form stable OsX_4 compounds. Similarly, T(IV) should also act as a Lewis acid and TX_4 should be a stable compound. As expected, TX_4 compounds ($X = F, Cl, Br, OH, SH, CN \dots$) were calculated to be very stable with large HOMO-LUMO gaps and VIPs (see Figure S3 in Supporting Information). AdNDP analysis shows that the electronic configuration of T in TX_4 is similar to that in TM_4 , where T is also in D^3S hybridization bonded with four p_z

orbitals of X. Taking TCl_4 as an example, Fig. 5a plots the four AdNDP localized super T-Cl bonds (D^3S-3p_z), which are obviously similar to the Os-Cl bonds (d^3s-3p_z) of $OsCl_4$ in orbital shapes (Figure 5b).

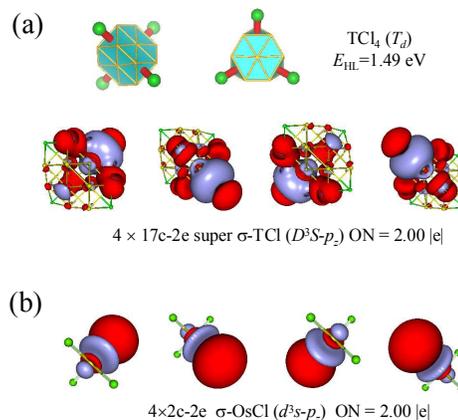


Figure 5. (a) Superatomic-molecule models and four AdNDP localized super T-Cl bonds of $Au_{16}Cl_4$ (TCl_4), and (b) four AdNDP localized Os-Cl bonds of $OsCl_4$.

The reaction energy of $4/5 Au_{20} + 2 X_2 \rightarrow TX_4$ are calculated to be very large: F(-7.70 eV) > Cl(-5.29 eV) > Br(-4.89 eV), which indicates TX_4 is thermally more stable than bare Au_{20} . Moreover, TF_4 is the most stable and T(IV) acts as a very hard Lewis acid. Thus, chemical property of T is very different from that of Au element which often acts as a soft Lewis acid.

The predicted TM_4 and TX_4 superatomic molecules are real local minima in the potential energy surface (PES) verified by the absence of imaginary vibrational modes. Are these molecules global minima in PES? Taking $Au_{16}Cl_4$ as a test case, we perform an unbiased global minimum search of the PES using the method of genetic algorithm plus density functional theory. In the global search, over 600 minima are relaxed by DFT. The TCl_4 superatomic molecule is successfully located in the unbiased search as the global minimum one and is 0.49 eV lower in energy than the second isomer (see Figure S4 in Supporting Information).

The T-Au super bond in TAu_4 is nearly nonpolar. NBO analysis reveals that the polarity of T-Au bond is about 51%:49%. However, other T-M and T-X bonds may be in great polarity. The polarity of T-Na and T-Cl bonds are 93%:7% and 15%:85%, respectively. On the other words, TNa_4 can be viewed as $T^{4-} \cdot 4Na^+$ and TCl_4 is $T^{4+} \cdot 4Cl^-$, where T-Na and T-Cl super bonds are mainly ionic and T is a Lewis acid in the former and Lewis base in the later. T^{4+} may be the global minimum structure, and is 1.14 eV lower in energy than the -4 ion of the C_{2v} flat cage. However, T^{4+} is 0.10 eV higher in energy than the +4 ion of the C_{2v} structure. The bare T^{4+} and T^{4-} ions are not as stable as in the compounds, where the calculated HOMO-LUMO gaps are only 0.92 eV and 1.10 eV, respectively, much lower than those of $T^{4+} \cdot 4Cl^-$ (1.49 eV) and $T^{4-} \cdot 4Na^+$ (1.61 eV). This is due to the D^3S hybridization of T, which is greatly stabilized in the tetrahedral field of $4Cl^-$ or $4Na^+$. Geometry of the 3D superatoms should satisfy the

hybridization of superatomic orbitals different from the orbital hybridization of atoms, where each atom is taken as a 0D point. Thus, T is a magic number tetravalent superatom in tetrahedral geometry instead of spherical in the tetrahedral coordination with D^3S hybridization.

It is noticeable that 20e is the magic number of sodium clusters in spherical Jellium model. However, the magic number is 18e for Au clusters due to 6s character, where $[Cu@Au_{16}]^-$ and $Zn@Au_{16}$ are viewed as 18e close-shell superatoms.³¹ Evidences can be given from the geometries of T^{4+} , T^{4-} and T^{2-} . T^{4+} and T^{4-} maintain the tetrahedral geometry in TAu_4 , however, T^{2-} tends to be a spherical cage due to the spherical Jellium effect of 18e. Moreover, the HOMO-LUMO gap of the spherical 20e $[Cu@Au_{16}]^{3-}$ (0.73 eV) is also much lower than that of the spherical 18e $[Cu@Au_{16}]^-$ (1.21 eV), indicating a 18e shell closure (all in Figure S4 in Supporting Information). Thus, the magic electronic stability of TAu_4 is due to the superatom-atom bonding instead of the spherical Jellium effect.

In summary, we revisit the electronic structure of Au_{20} cage (T_d) based on the recently proposed SVB model. Au_{20} is proved to be a superatomic molecule (TAu_4) bonded by one 16c-16e Au_{16} superatom and four Au atoms and is an exact analogue of OsH_4 molecule. Clear evidences for the T-Au superatom-atom super bonding are given by comparing the MO diagrams and AdNDP bonding patterns of TAu_4 and OsH_4 . Moreover, based on our model, TX_4 ($X = F, Cl, Br, OH, SH, CN...$) are predicted to be very stable, where T(IV) acts as a hard Lewis acid different from the chemical property of Au element. In closing, we believe that such a superatom-atom super bonding gives a new physical insight in chemical bonding and enriches the continents of chemistry. And new molecules/compounds and materials can be designed based on such a superatom-atom super bonding.

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† Electronic Supplementary Information (ESI) available: Computational details, AdNDP chemical bonding of ten 10c-2e bonds of Au_{20} , and optimized structures of TM_4 and TX_4 , low-lying isomers of TAu_4 , and geometries of T^{4+} , T^{4-} , T^{2-} , $[Cu@T]^-$ and $[Cu@T]^{3-}$. See DOI: 10.1039/b000000x/

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